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TECHNICAL REPORT

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THE REACTION OF ATOMIC HYDROGEN WITH FORMALDEHYDE

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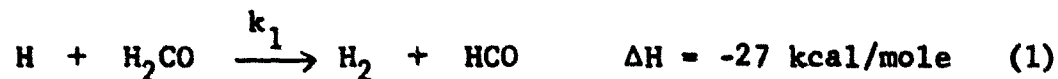   Washington, D. C.

THE REACTION OF ATOMIC HYDROGEN WITH FORMALDEHYDE

The reaction of hydrogen atoms with formaldehyde is of importance in both the photolysis[1,2,3] and the pyrolysis[4] of formaldehyde. It has been postulated also to occur in formaldehyde oxidation.[5] The rate of the reaction has been estimated from the results of the pyrolysis reaction,[4] and the relative rates of the reactions of atomic hydrogen with formaldehyde and deuterium have been measured by photolysis of formaldehyde, deuterium mixtures.[2,3] No direct measurement has been made, however, since 1936 when Geib[6] estimated the activation energy for this reaction to be less than 5.7 kcal/mole.

We have studied the reaction directly in a fast flow system. Hydrogen atoms were generated with a microwave discharge in a 10% mixture of molecular hydrogen in helium at a pressure of 1 - 2 mm Hg, and formaldehyde was admitted to the reactor downstream of the discharge. The course of the reaction was followed with a time-of-flight mass spectrometer. Details of the apparatus and techniques used have been published previously.[7] Gaseous formaldehyde was produced by distillation from polyoxymethylene, stored at $60^{\circ}C$ in a heated 1 liter pyrex bulb and handled in heated lines.

The only major product observed was carbon monoxide. Under all conditions studied the number of molecules of carbon monoxide formed was equal to the number of molecules of formaldehyde that had reacted. The only other possible product, molecular hydrogen, could not be observed above the large excess of undissociated hydrogen remaining after the discharge.

The reaction was found to be first order in both atomic hydrogen and formaldehyde concentrations and can be represented well by the following scheme:

$$H + H_2CO \xrightarrow{k_1} H_2 + HCO \qquad \Delta H = -27 \text{ kcal/mole} \qquad (1)$$

$$H + HCO \xrightarrow{k_2} H_2 + CO \qquad \Delta H = -81 \text{ kcal/mole} \qquad (2)$$

provided the rate of reaction (2) is greater than that of reaction (1). At room temperature the unimolecular decomposition of HCO, which occurs at higher temperatures,[2,3] is too slow to be of importance.[8]

Figure 1 shows $\log_{10}$ [H_2CO] plotted as a function of the distance between the formaldehyde inlet and the mass spectrometer pinhole in two mixtures, both containing a sufficient excess of atomic hydrogen for its concentration to remain almost constant throughout the reaction. Since the linear flow speed is constant, this distance is proportional to the time of reaction. The ratio of the hydrogen atom concentrations present in these two experiments was 1.95. The ratio of the slopes was measured as 1.96, which shows that the reaction is first order in hydrogen atoms as well as in formaldehyde. Figure 2 (a) shows a similar plot of the decay of atomic hydrogen concentration in a mixture containing a very large excess of formaldehyde. The rate constant k_1 was estimated from such plots to be $(4.4 \pm 1.2) \times 10^{-14}$ cc/molecule-sec. A 15% correction has been applied to this value to account for the effect of diffusion of hydrogen atoms. The correction was estimated by a procedure similar to that used by Schulz and LeRoy.[9] A graph of both hydrogen atom concentration and ($[CO]_\infty$ - $[CO]$) as a function of reaction time is shown in Fig. 2 (b) on a semi-log scale. The subscript ∞ indicates an extrapolation to infinite reaction time. Since the two curves are parallel, the rate of formation of CO must be equal to the rate of removal of hydrogen atoms. This shows that reaction (2) is fast compared to reaction (1) and that

very little formaldehyde is reformed by addition of hydrogen atoms to HCO.

Our value for the rate constant is smaller than the value of 4×10^{-13} cc/molecule-sec. obtained by extrapolation of the photolysis data[3] from $600^\circ K$. This suggests that the activation energy may be slightly higher than the value of 2.0 kcals/mole given previously.[3]

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FIGURE CAPTIONS

FIGURE 1   The concentration of formaldehyde as a function of reaction time for two mixtures containing a large excess of atomic hydrogen.

FIGURE 2   The concentrations of various reactants and products as a function of reaction time in formaldehyde rich mixtures. Linear flow speed = 640 cm/sec. In (a) $[H_2CO] = 1.1 \times 10^{15}$ molecules/cc. In (b) $[H_2CO] = 7.5 \times 10^{14}$ molecules/cc.

8

$(HCHO)$

6

$[(CO)_\infty - (CO)]$

4

2

(H)

(b)

8

6

(a)

4

(H)

2

RELATIVE CONCENTRATION

DISTANCE IN CM

2 4 6 8 10 12 14